InTlSb REPORT

InTlSb for Long-Wavelength Infrared Photodetectors and Arrays

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Manijeh Razeghi

Center for Quantum Devices

Dept. of Electrical Engineering and Computer Science

Northwestern University

Evanston, Illinois 60208

MBE material growth and characterization:

Dr. I. Ferguson

Erick Michel

Gurpreet Singh

Status report for the growth of InSb by Molecular Beam Epitaxy

SUMMARY OF ACHIEVEMENTS

- New solid source molecular beam epitaxy system successfully installed and commissioned.

- The first observation of InSb both In-induced and Sb-induced RHEED oscillations obtained for InSb nucleated onto a GaAs substrate.

- An InAs layer of thickness 3.5 μm was grown onto GaAs had a X-ray rocking curve FWHM of 204 arcsec and a Hall mobility of 3.8×10^4 cm^{2}V^{-1}s^{-1} at 77K, comparable with the best reported elsewhere.

- InSb nucleated directly onto GaAs had a X-ray rocking curve FWHM of 183 arcsec, the best reported for this material nucleated directly onto GaAs. In addition, the measured Hall mobility of 8.2×10^4 cm^{2}V^{-1}s^{-1} for a 3.3 μm thick layer is again the best reported for InSb nucleated directly onto GaAs. The InSb grown in this work did not require the use of low temperature Atomic Layer Epitaxy or an AlSb buffer layer to improve the properties of the interface.

1. INTRODUCTION

A number of samples have been grown in the Intevac-EPI solid-source Molecular Beam Epitaxy (MBE) system since it was first commissioned in early May, 1994. The samples have consisted of both undoped and doped InSb, undoped InAs and various calibration layers such as n-type and p-type GaAs doping staircases. The different surface reconstructions and surface phase transitions have been investigated using Reflection High Energy Electron Diffraction (RHEED). For example, InSb growth temperature is set relative to a c(4x4) to a(1x3) surface phase transition, corresponding to an actual surface temperature of 390°C. RHEED oscillations were observed for GaAs, InAs and InSb as this is particularly important for determining growth rates and III/V flux ratio. The philosophy has been to determine system independent growth parameters so that the technology can be easily transferred to other growth systems. InSb X-ray linewidths of 183 arcsec and mobilities of $\approx 80,000$ cm^2/V-sec for a 3 μm thick layers are the best reported to date.

2. COMMISSIONING OF THE MBE SYSTEM

The Intevac-EPI MBE system was delivered February 1994 and installation was not completed until April 1994 because a chiller system was not delivered until that time. This is the first MBE system that EPI has been responsible for commissioning since they bought InteVac. The use of the chiller system to provide thermal isolation between the effusion cells is being investigated as alternative to the more costly option, liquid nitrogen. A number of other problems were resolved during the commissioning of the system. These include replacing the hard disk on the Pinnacle computer system that crashed, possibly due to a power outage. Additionally, the growth chamber ion pump gate valve had to replaced because the valve shaft broke after a few operations. Typically, if high vacuum components do not fail after being baked, they will operate for extended periods.

A number of new effusion cells were ordered and installed for the antimony and thallium sources. The use of antimony is particularly problematic because the vapor pressure is such that sufficient fluxes for growth require the effusion cell to be operated at temperatures close to the melting point of antimony. This normally results in the deposition of antimony around the lip of the cell or on the shutter that eventually makes the cell inoperative. A hot-lipped cell provides a thermal gradient along the length of the crucible that helps to minimize this problem. The Intevac-EPI system has four downward looking cells which means only four liquid sources can normally be used, in this case gallium, indium, aluminum and antimony. The thallium is also liquid so a special crucible to allow its use downward looking configuration was installed.

It was necessary after the installation of the new effusion cells and empty crucibles to complete a rigorous program of outgassing before the source materials were loaded. The process of outgassing

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Center for Quantum Devices (CQD)
Dr. Manijeh Razeghi, Director

June 1, 1994

Dr. Yoon-Soo Park
Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217-5660

Dear Dr. Park:

Please find enclosed copies of our annual report for the three
separate projects which we have supervised by you, Dr. George
Wright, and Dr. Ray Balcerak at ARPA.

Please feel free to contact me if you have any questions or need
additional information.

Best regards,

Manijeh Razeghi
Walter P. Murphy Professor and
Director, Center for Quantum Devices

MR:gm

Enc.

cc: Dr. G. Wright
     Dr. R. Balcerak

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     Dr. R. Balcerak

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Center for Quantum Devices (CQD)
Dr. Manijeh Razeghi, Director

June 1, 1994

Dr. Ray Balcerak
Advanced Research Projects Agency
3701 N. Fairfax Drive
Arlington, VA 22203-1714

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     Dr. G. Wright

is particularly important for narrow semiconductor materials since even a relatively small concentration of impurities can radically change the properties of the material produced. The cells were outgassed according to the recommendations in the Intevac-EPI instruction manuals. Following this initial outgassing the source material was then loaded and the complete system was baked for an extended period of time. Since the dopants were to be located in a downward looking location, they had to be premelted before being installed. Once the system bakeout was completed, each cell was individually outgassed and precalibrated using a Beam Monitoring Ion Gauge (BMIG).

Following the commissioning of a new MBE system a series of calibration layers are grown to coat the interior of the growth chamber in order to minimize any changes in emissitivity during growth. Generally this is done by growing thick doped layers of GaAs with decreasing levels of doping concentration with each subsequent growth. Finally an undoped GaAs layer is grown that gives an indication of the operational characteristics of the system and the purity of the source materials. However, since the system installed in this laboratory is meant to primarily grow InSb based compounds it made little sense to commission the system for GaAs based growth. So following the growth of two GaAs layers relatively thick InSb layers were grown.

3. RESULTS

Substrate preparation

The substrate quality and cleaning process is important since the grown epilayer quality depends critically upon them. Recently, the trend has been to use epi-ready material that is put directly into the growth system without any substrate preparation. This relies on the substrate manufacturer completing the correct etch to remove polish damage. This technology is only typically available for GaAs substrates. In general, the substrate cleaning procedure depends on the material type with the etch chosen accordingly. The substrates are solvent degreased by boiling in trichlorethlyene, acetone and then methanol. The methanol is water soluble and when the substrate is rinsed in HPDI water, the surface is normally hydrophilic in nature. For GaAs and InSb, H_2O_2/H_2SO_4 and a modified CP4A etches have been used, respectively. After etching, the substrate was thoroughly rinsed and blown dry with nitrogen before mounting with molten indium onto the molybdenum substrate holder. It is important to ensure a good thermal contact between the substrate and substrate holder for growth reproducibility.

For simple GaAs growth, the substrate was raised to the growth temperature under an arsenic flux to minimize any non-congruent evaporation at the surface. At ~585 °C the native oxide on the epi-ready material or the oxide formed during the etch desorbs, leaving the substrate clean and ready for

growth. RHEED is used to monitor the thermal cleaning of the substrate and to determine oxide desorption temperature, T_{od}. System independent variables such as T_{od} provide a measure of the temperature of the sample surface independent of the thermocouple temperature. The emissivity of a particular substrate and the substrate holder can vary depending on the recent history of the substrate holder. An attempt to thermally desorb the oxide on InSb, which had been etched using the modified CP4A etch, failed. The indium oxide on the surface was thermally stable and the substrate melted. Alternative etches which result in a less thermally stable indium chloride based oxide will be investigated.

Surface phase transitions

Different surface reconstructions can be maintained over a large range of flux ratios and growth temperatures. Surface phase diagrams have proved to be a powerful tool in mapping out the surface reconstructions during both Langmuir evaporation and growth. This has helped in the identification of the optimum growth conditions for many different material systems. For example, the growth of high quality GaAs on a [100] substrate is normally achieved under an As stabilized (2x4) reconstruction at a growth temperature of 580°C and a J_{As_4}/J_{Ga} flux ratio of greater than four. It should be stressed that there is no simple relationship between the material quality and surface reconstruction. Models suggest that the (2x4) reconstruction is relatively insensitive to surface stoichiometry since arsenic coverage can vary by 50-75%.

However, the transitions between different surface reconstructions are clearly defined, especially during Langmuir evaporation. For example, the c(4x4) to (2x4) reconstruction is observed for an (001) GaAs surface at ¯515°C and is relatively insensitive to arsenic flux. This has been used to provide another independent measure of the surface temperature during growth. For each substrate holder differences in the emissitivity result in the surface phase transitions occurring at different temperatures. Surface phase transitions have been used as a relative measure of the substrate temperature rather than the thermocouple temperature. This has proved particularly important for InSb because a transition between a c(4x4) to a(1x3) reconstruction on (001) InSb at ¯390°C occurs almost at the optimum growth temperature for this material. If InSb is grown heteroepitaxially on GaAs the growth temperature is approximately 200°C from T_{od}. This results in a large error if the thermocouple is used to measure the temperature. In general, all growth temperatures are stated relative to a surface phase transition at a particular group V flux.

It has also been found to be relatively simple to freeze surface reconstructions on the (001) InSb surface that are normally only observed at high growth temperatures. The a(1x3) reconstruction is only observed above 390°C at normal antimony fluxes. On terminating growth, if the sample is turned away from the antimony source so that no antimony can accumulate on the surface, the

a(1x3) reconstruction is observed even at room temperatures. This is important because in an attempt to relate the plethora of surface reconstructions observed in different material systems the concept of domain structures has been used to develop an universal model. Different coverage of the group V element (50-75%) may explain the variation in spacing between the a(1x3) reconstruction on (001) InSb. Since this reconstruction can be easily obtained at room temperature, it can be probed by Scanning Tunneling Microscopy.

RHEED Oscillations

Temporal variations can be observed in the intensity of the diffraction features in the RHEED pattern during growth. When the specular spot is monitored, it shows a characteristic periodic oscillation reflecting the two dimensional nucleation and growth of a monolayer of GaAs on the (001) GaAs surface. A simple kinematic model can be used to understand the origin of the oscillations. Before growth, the RHEED beam diffracts from a smooth, singular surface. When growth is initiated, a periodic roughing of the surface occurs due to layer by layer growth mode of MBE and diffuse scattering is a maximum at 50% coverage when the oscillation period is a minimum. RHEED oscillations can be used to measure the effective incorporation rates of both group III and group V species, to explore adatom surface migration lengths, and toprobe interface quality and growth mechanisms.

RHEED oscillations have been obtained during the growth of GaAs and InAs, subsequently nucleated onto a GaAs substrate. RHEED oscillations give an accurate measurement of the incorporation of the group III element which, is directly proportional to the flux incident on the surface if the sticking coefficient is unity. Oscillations have been observed over a period of minutes for the growth of GaAs with no evidence of beating due to flux uniformities.

RHEED oscillations provide a much more accurate method of calibrating InSb growth during MBE rather than using BMIG measurements. We have found that large errors can occur in BMIG measurements depending on the recent history of the ion gauge. RHEED oscillations provide a direct measurement of the incorporation of indium and antimony at the surface of the growing InSb. This is critically important for the growth of InSb because the vapor pressure of antimony is similar to that of indium. Growth cannot take place with a large excess group V flux like GaAs because the additional antimony will accumulate on the surface and will either desorb or incorporate into the growing film.

The sticking coefficient of the group V is seldom unity and indeed is frequently zero in the absence of a group III flux. A different procedure is therefore used to calibrate group V element fluxes (dimers or tetramers) and incorporation rates. In the case of GaAs, a known excess of the gallium is

first deposited on the substrate surface, with no arsenic flux present. This leads to the formation of isolated islands of gallium. Intensity oscillations are then induced by the arsenic flux and they continue until all of the surface excess of gallium has been consumed. Using the same technique to calibrate group V incorporation above, Sb_4-induced RHEED oscillations were observed following the controlled deposition of ~10 monolayers of indium onto a (001) InSb epilayer that had been nucleated onto a GaAs substrate. The period of the oscillation gives an accurate incorporation rate for antimony on InSb. A systematic calibration of Sb_4 incorporation was completed as a function of the antimony cell temperature at a constant substrate temperature of T_t-30°C and is shown in the form of Arrhenius plot in figure 1.
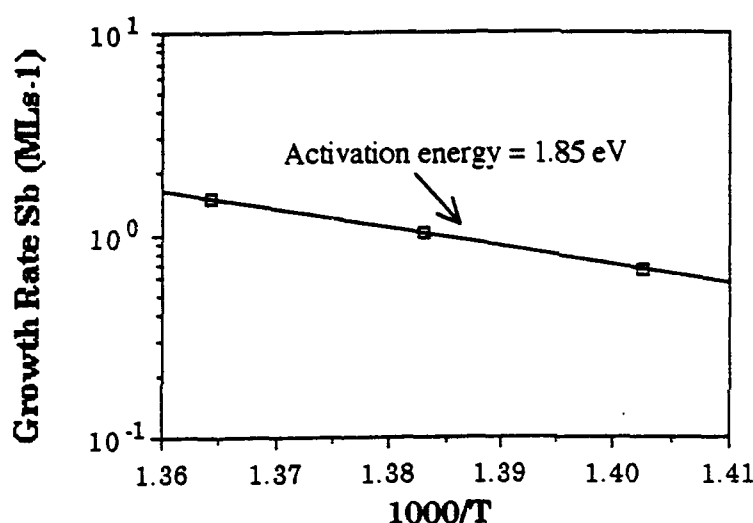

Figure 2:   An Arrhenius plot of the apparent activation energy of Sb_4 sublimation for a hot lipped effusion cell, 1.85 eV (solid line), obtained from Sb-induced oscillations.

The apparent activation energy of sublimation for Sb_4 was E_{Sb}=1.85 eV. Since the activation energy for the sublimation of antimony over antimony is 1.38 eV, this suggests the vapor pressure of antimony from the effusion cell has been measured. The slight difference in the in the measured and theoretical value is due to the construction of the hot lipped cell. The hot lipped cell is heated at the lip, as the name implies, so the thermocouple at the rear of the cell only measures a part of some average value. It is interesting to note that there is some is evidence that the sticking coefficient of antimony is unity even when Sb_4 is used and this will be investigated further.

Calibration layers

Calibration layers are primarily required for measuring the flux from the dopant cells since the RHEED oscillation method can not be used. In the process of commissioning the MBE system, a number of Si doped GaAs layers were grown that provided a rough measure of dopant concentrations from the dopant cell. The traditional method of calibrating the dopant cells is to CV (Capacitance-Voltage) profile a n-type or p-type doping staircases in GaAs. The dopant staircase is grown with a series of dopant steps of decreasing concentration and increasing thickness. Once this sample has been profiled, the dopant concentration can be normalized to a deposition rate of 1 MLs^{-1} for GaAs. The resulting Arrhenius plot gives the magnitude of the flux from dopant cell that can easily be corrected for changes in growth rate or lattice parameter when other material systems are grown. Again, the apparent activation energy of sublimation for the dopant is measured for the sublimation of silicon over silicon or beryllium over beryllium, figure 2. It is normal to recalibrate the dopant cells when the system has been opened.
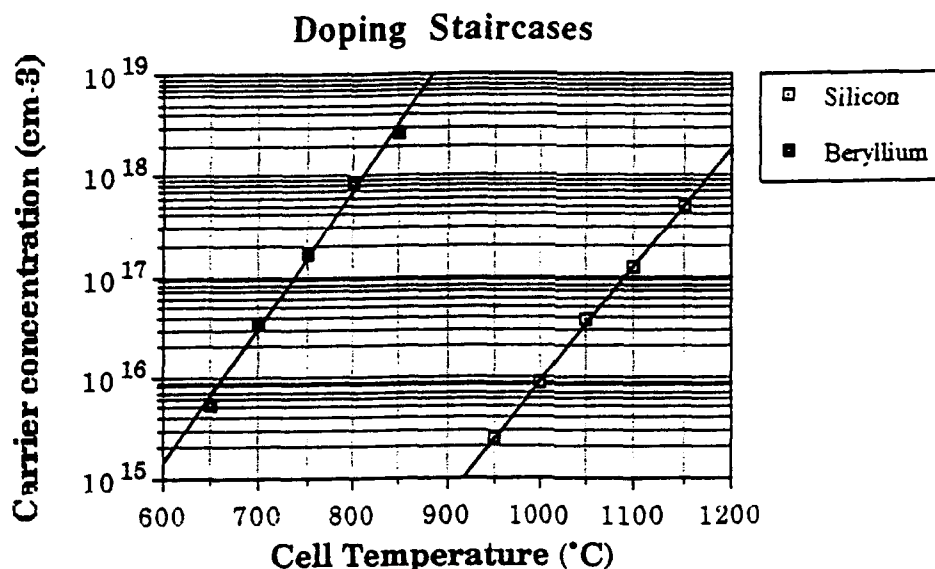
Doping Staircases

Figure 2:   CV profile of a silicon and beryllium doped staircase in GaAs.

Growth of undoped InAs

In order to check the purity of the individual source materials it is necessary to grow a whole matrix of different binary compounds such as GaAs, GaSb, InAs and InSb. For this reason a layer of InAs was grown as close as possible to the optimized growth conditions for this material system. The quality of the InAs critically depends on the growth temperature rather than the In/As flux ratio. High mobility InAs is normally grown at ~490°C, which is close to the (2x4) to (4x2) surface phase transition. Unfortunately this results in a layer with a rough morphology because the (4x2) reconstruction is due to an indium terminated surface and desorption of indium may be occurring.

A layer of thickness 3.5 μm was grown and this was confirmed by both etching and ball polishing measurements. A sharp intense peak was observed in the (004) reflection of the X-ray rocking curve of Full Width Half Maximum (FWHM) of 204 arcsec. The measured Hall mobility and carrier concentration of 1.2 x 10^4cm^{2}V^{-1}s^{-1} and 9 x 10^{15} cm^{-3} at 300 K and 3.8 x 10^4cm^{2}V^{-1}s^{-1} and 5 x 10^{15} cm^{-3} at 77K are comparable with the best reported elsewhere. It should be stressed that it is difficult to do simple a comparison of Hall mobility due to the existence of a two-dimensional surface accumulation layer. However, the result is very promising considering that this was only the third layer to be grown in the new MBE system.

Growth of high quality undoped InSb

The new MBE system has been specifically commissioned to grow InSb based compounds. At first, it is necessary to show the ability of the MBE system to grow high quality InSb layers. Hence, a series of undoped InSb layers have been grown to optimize the structural, electrical and optical properties of this material. The system independent parameter of T_t and the observation of RHEED oscillations have been used to calibrate the growth conditions. To date, InSb has been grown at temperatures around T_t and In/Sb flux ratios of 1.88 and 1.25. These growth conditions are known to produce the best quality material. All the InSb layers have been grown heteroepitaxially onto Semi-insulating GaAs substrates. The epilayers have been grown with the same nominal thickness of 3.3 μm because both the structural and electrical properties depend strongly on thickness. The FWHM of the x-ray peaks have a strong correlation with the number of dislocations. Therefore, as the layer thickness increases the FWHM decreases. The mobility measurements also depend on thickness because one or possibly two channels of parallel conduction exist that are independent of layer thickness. Therefore, as the layer thickness increases, the mobility increases. The important data obtained to date is summarized in Table 1 below.

Table 1: Undoped InSb sample data

Sample #	Temperature (T_t = 390°C)	Flux ratio (In/Sb)	X-ray (arcsec)	μ at 300K (cm^{2}V^{-1}s^{-1})	n at 300K (cm^{-3})	μ at 77K (cm^{2}V^{-1}s^{-1})	n at 77K (cm^{-3})
ssmbe005	T_t+ 5°C	0.8/1.5	292	21600	3.6 x 10^{17}	30600	1.1 x 10^{17}
ssmbe008	T_t+ 30°C	0.8/1.5	183	40500	5.9 x 10^{16}	35000	4.9 x 10^{16}
ssmbe010	T_t + 5°C	0.8/1.0	193	59400	2.7 x 10^{16}	81500	1.7 x 10^{16}

The results in Table 1 are remarkable considering that they were achieved from the first few layers grown by this system. The InSb was nucleated directly onto GaAs without the use of low temperature Atomic Layer Epitaxy or an AlSb buffer layer to improve the interface.
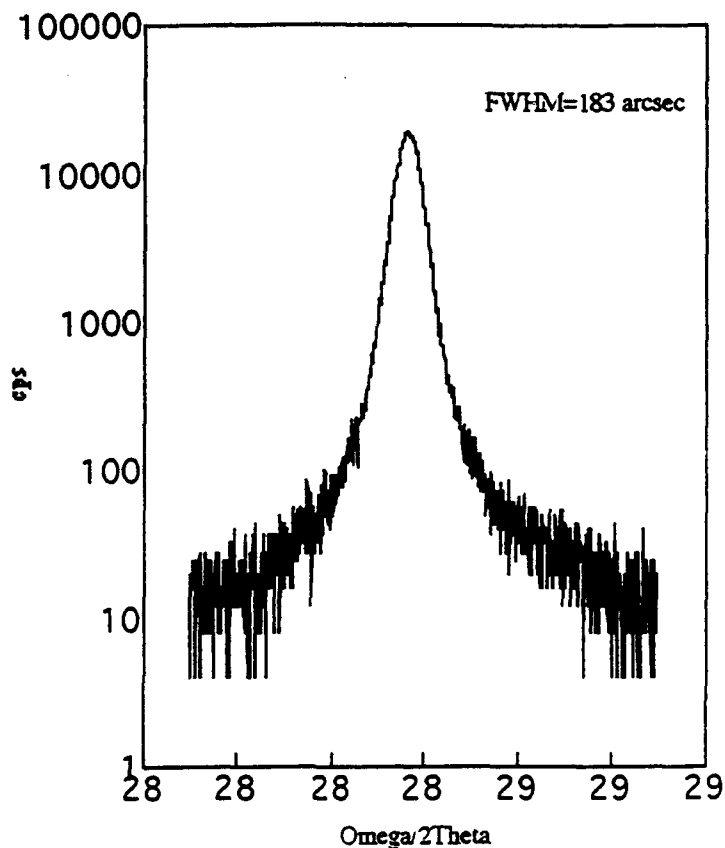

Figure 3: The (004) reflection of the X-ray rocking curve of an InSb layer nucleated directly onto GaAs.

The measured FWHM of 183 arcsec is the best reported for InSb nucleated directly onto GaAs, figure 3. In addition, the measured Hall mobility of $8.2 \times 10^4\,cm^2V^{-1}s^{-1}$ for 3.3 μm thick layer is also the best reported for InSb nucleated directly onto GaAs, figure 4.
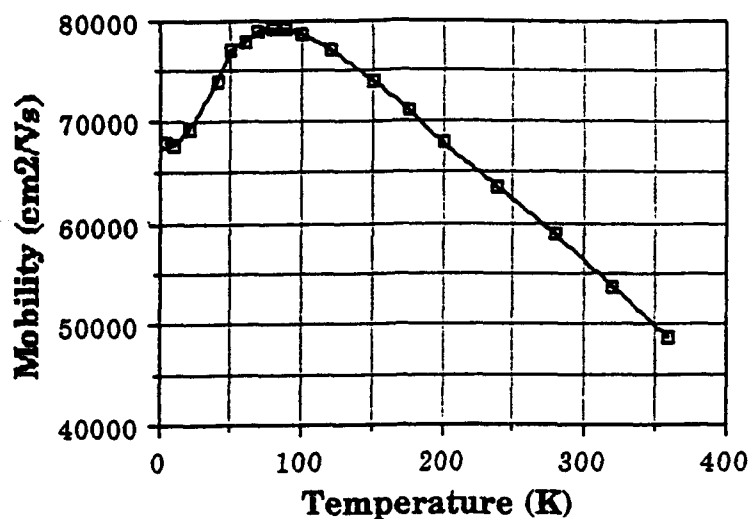
Figure 4: Temperature Hall mobility of InSb for 3.3 μm thick layer nucleated directly onto GaAs, sample ssmbe010.

Growth of doped InSb

Some silicon and beryllium doped layers of InSb have also been grown in preparation for PIN photodiode structures. These are generally the best behaved and most commonly used shallow acceptor and donor dopants in MBE growth. The silicon behavior is complicated because it is a group IV element, and is amphoteric in nature. This is particularly true at the high doping levels and high growth temperatures, $T_t + 30$ °C. The highest doping levels reported for InSb are 3-5 x 10^{18} cm^{-3} for growth temperatures of T_t-40° C, however; if the growth temperature is too low the silicon is not electrically active. For doping levels of <10^{18} cm^{-3} silicon is non-amphoteric favoring the In site if the growth temperature is kept below T_t. To date, InSb (ssmbe011) has been grown with a silicon doping concentration of 2 x 10^{18} cm^{-3} at a growth temperature of T_t-30 °C. No attempt has been made to optimize the growth for higher doping concentrations at this time. The beryllium permits controllable doping levels between 10^{15} to 10^{19} cm^3 with 100% electrically active centers. InSb has also been grown with a beryllium doping concentration of 2 x 10^{18} cm^{-3} at a growth temperature of T_t-30 °C.

4. PROJECTED WORK

- Complete the optimization of InSb growth by further reducing the X-ray linewidth and increase the Hall mobility for heteroepitaxial growth on GaAs.

- Complete a study of the n type InSb doping calibration.

- The growth of large area InSb detector structures on silicon substrates.

- The growth of InTlSb.

- The growth of GaInAsSb and AlGaAsSb lattice matched to GaAs for laser structures.